

# PATENT SPECIFICATION

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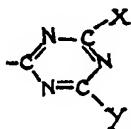
The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act 1949 are HANS BAUMANN, HARRY DISTLER, KARL MERKEL, ARNOLD TARTTER, HERMANN WEISSAUER and HEINZ-ULRICH WERNER, citizens of Germany and residents, respectively, of 8 Alwin-Mittasch-Platz, Ludwigshafen/Rhein, Germany; 4 Alwin-Mittasch-Platz, Ludwigshafen/Rhein, Germany; 1 Ebertstrasse, Ludwigshafen/Rhein, Germany; 47 Hauptstrasse, Lambsheim, Germany; 6 Alwin-Mittasch-Platz, Ludwigshafen/Rhein, Germany; 24a Woehlerstrasse, Ludwigshafen/Rhein, Germany.

## COMPLETE SPECIFICATION

### New Dyes of the Tetrazaporphin Series

We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of Ludwigshafen/Rhein, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new, preferably water-soluble, tetrazaporphin dyes which contain, attached by way of an amino group, at least one group of the general formula:



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in which X denotes hydrazine or a hydrazine substituted by alkyl or acyl groups, and Y denotes a chlorine or a bromine atom, a hydroxyl group, a sulphydryl group, a sulphonic acid group, a primary, secondary or tertiary amino group, an ether group, a thio ether group or the radical of a hydrazine or substituted hydrazine. Furthermore, the invention relates to a process for the production of such dyes.

The secondary or tertiary amino groups, the ether groups, the thioether groups or the substituted hydrazine groups may be of aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic nature and may bear further substituents. They may be present especially, for example as low molecular weight alkylamino,

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alkyl ether or alkylthioether groups, such as monomethylamino groups, dimethylamino groups, ethoxyl groups, tert-butymercaptop groups, diethanolamino groups, isopropylamino groups or n-butylamino groups. Suitable aromatic groups include amino, ether and thioether groups which contain one or two benzene rings, such as phenoxy groups, o-, m- or p-chloranilino groups or o-, m- or p-toluidino groups. Cycloaliphatic, araliphatic or heterocyclic amino, ether or thioether groups include phenylethyl ether groups, N-cyclohexyl amino groups or benzothiazolyl thioether groups.

We have found that these valuable dyes of the tetrazaporphin series are obtained when one mole of 2,4,6-tribromo- or trichloro-1,3,5-triazine is reacted at temperatures of up to 40°C. in any sequence with (a) one mole of a tetrazaporphin dye, preferably soluble in water, which contains at least one primary or secondary amino group, and (b) one mole of hydrazine or a hydrazine substituted by alkyl or acyl groups to form a binary condensation product, the halogen atom present in the triazine ring is, if desired, substituted in the usual way by a hydroxyl group, a sulphydryl group, a sulphonic acid group, a primary, secondary or tertiary amino group, a thioether group or the radical of hydrazine or a substituted hydrazine.

Water-soluble dyes are preferred for the reaction of cyanuric chloride or bromide, with tetrazaporphin dyes containing primary or secondary amino groups. These compounds preferably contain water-solubilising groups which dissociate to give an ion of an acid,

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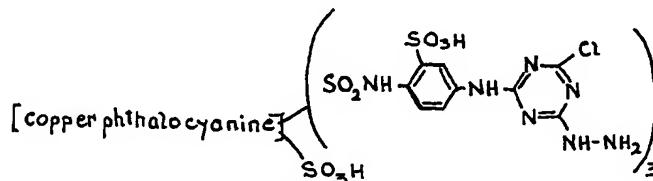
5	such as sulphonic acid groups, carboxylic acid groups, sulphuric acid ester groups or arylcarboxylic acid ester groups which bear at least one sulphonic acid group attached to the aryl radical.	The reaction of the 2,4,6-trihalogen-1,3,5-triazines with tetrazaporphin dyes containing primary or secondary amino groups and with hydrazine or substituted by alkyl or acyl groups may be carried out in the usual way in any sequence in water or in organic solvents, for example in alcohols, such as ethanol, in ketones, such as acetone, in polar solvents, such as N,N-dimethylformamide or N-methyl pyrrolidone, or mixtures of the same with each other and/or with water and advantageously in the presence of acid-binding agents, for example alkali metal acetate, carbonates or hydrogen carbonates, such as sodium acetate, potassium carbonate or sodium bis-carbonate.	70
10	Tetrazaporphin dyes containing primary or secondary amino groups may be derived from tetrazatetrazenophorphins, as for example from metal-free phthalocyanine or from iron, cobalt, nickel or aluminium phthalocyanine, especially from copper phthalocyanine, or from substituted tetrazatetrazenophorphins, for example phthalocyanines of a low degree of halogenation, such as mono-, di- or tetra-	In the binary condensation products containing, attached by way of an amino group, the group of the above general formula I in which X denotes the radical of hydrazine or a hydrazine substituted by alkyl or acyl groups, and Y denotes a chlorine or bromine atom, the halogen atom Y attached to the triazine ring may be exchanged for an OH— group by hydrolysis, or for a sulphydryl group, a sulphonic acid group, a primary, secondary or tertiary amino group, an ether or thioether group, a radical of hydrazine or a substituted hydrazine by treatment at temperatures of up to 100°C with a metal sulphite or a metal sulphide, ammonia, primary or secondary aliphatic or aromatic amines or their sulphonic acids, aliphatic or aromatic alcoholates or mercaptans, hydrazines or hydrazine derivatives.	75
15	chlor copper phthalocyanines, from alkylated or arylated phthalocyanines, such as di-, tetra- or octa-phenyl copper phthalocyanines, or from phthalocyanines containing benzoyl, phenoxy, phenyl-mercapto or phenylsulphonyl copper phthalocyanine. Azaphthalocyanines or naphthaphthalocyanines, and also tetrazaporphins which contain less than four or no benzo rings, for example tetramethyl-tetraphenyl- or octaphenyl-nickel or -copper	90	
20	25	tetrazaporphins, tetramethyl- or tetraphenyl-tetrazadibenzoporphins may also form the basis of the said tetrazaporphin derivatives.	95
30	The following compounds are examples of initial dyes of the tetrazaporphin series: tetramino copper phthalocyanines or tetrakis-(aminomethyl) copper phthalocyanine, further tetrazaporphin derivatives which contain water-solubilising groups, especially sulphonic acid groups, in the molecule, for example	In the form of their methylol compounds, which are obtained in the usual way for example by reaction with formaldehyde, and also in the form of the corresponding methylene esters or ethers, the dyes obtainable according to this invention are eminently suitable for dyeing and/or printing material, for example textile materials, such as fibres, threads, flocks, woven fabrics and knitted fabrics of native and/or regenerated cellulose.	100
35	tetrakis-amino copper phthalocyanine tetrasulphonic acid, bis-, tris-, or tetrakis-amino-methyl copper phthalocyanine di-, tri- or tetrasulphonic acid, bis-p-aminobenzoyl, bis-p-amino-phenylmercapto or bis-p-amino-	105	
40	phenylsulphonyl copper phthalocyanine sulphonate acids or the tetrazaporphins containing methylenearyl radicals substituted in the aryl radical by hydroxyl, amino and sulphonic acid groups obtainable by the process known	110	
45	45 from British Patent Specification No. 827,569 by reaction of halogenmethyl tetrazaporphins with amino hydroxyarylsulphonic acids. Furthermore there may be used as initial materials tetrazaporphin derivatives containing amino groups which can be obtained by reaction of tetrazaporphin sulphonic acid chlorides with aromatic amino compounds which have at least one further amino group or at least one nitro or acylamino group, the nitro group being converted into a primary amino group in conventional manner, for example by reduction by means of sodium sulphide, or the acylamino group by splitting off the acyl radical.	115	
50	50 Hydrazines substituted by alkyl or acyl groups include methyl hydrazine, N,N <sup>1</sup> -dimethyl hydrazine, acetyl hydrazine, hydrazo-dicarboxylic acid amide, maleic acid hydrazide, phthalic acid hydrazide and N-amino-	120	
55	60	Furthermore, the new dyes or their methylol compounds may also be applied to the material to be dyed in the usual way in the presence of acids or acid-reacting compounds, for example salts of strong acids and weak bases, such as ammonium chloride, together with hardenable aminoplast-forming substances or the precursors of such substances, possibly together with aldehydes or compounds giving off aldehydes, for example	125
65	65 ethyl urethane.	130	

formaldehyde, and fixed by means of a heat treatment. This may be combined with a conventional treatment, for example a finishing treatment, such as creaseproofing chintzing or shrinkproofing. Obviously, levelling, wetting and hydrophobing agents, plasticisers and finishes as well as plastic dispersions may also be added in this process, and the dyed and/or printed materials may be subjected to a mechanical treatment, for example embossing, calendering, frictioning and possibly an after treatment at an elevated temperature. In this way, textile materials of natural, regenerated or synthetic fibres can be dyed or printed and finished in a single operation with the aid of the new dyes. With the dyes according to this invention the material can be dyed with excellent fastness to wet treatment in a few minutes and at the same time finished. With the conventional dyes a considerably longer time is necessary for this purpose.

The invention is illustrated by, but not limited to, the following Examples in which, unless otherwise stated, parts and percentages are by weight; parts by volume have the same ratio to the parts by weight as the litre, measured under standard conditions, has to the kilogram.

## EXAMPLE 1

40 parts of a dye obtainable by reaction of one mol of copper phthalocyanine-4,4<sup>1</sup>,4<sup>11</sup>,4<sup>111</sup>-tetrasulphonic acid chloride with three mols of 4-acetylaminoo-1-aminobenzene-2-sulphonic acid and subsequent saponification of the unreacted sulphonic acid chloride groups and splitting off of the acetyl radical, are dissolved in 300 parts of water, and neutralised. This solution is allowed to flow while stirring into a mixture, cooled to 0°C, of 16 parts of cyanuric acid chloride, 100 parts of tetrahydrofuran and 400 parts of water in small portions. Then the cooling means is removed and the temperature of the reaction mixture is allowed to rise to about 15°C. After a reaction period of five hours, 30 parts of an aqueous solution which contains 8.5 parts of hydrazine hydrate and 15 parts of crystallised sodium acetate dissolved therein are added and the mixture is stirred for about 20 hours. After adding 130 parts of potassium chloride, the deposited dye is filtered off by suction and dehydrated by washing with alcohol. Its sodium salt dissolved in water with a pure blue colour. The empirical formula of the dye suggests the following structure:

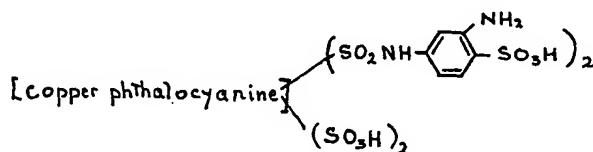


Cotton fabric is padded with an aqueous solution which contains in 1000 parts 20 parts of one of the above-mentioned dyes, 50 parts of 1,3-dimethylol-5-methylperhydrotriazole-(2) and 8 parts of monoammonium phosphate. After squeezing out and drying at 70°C, the fabric is heated for 7 minutes at 145° to 150°C. After soaping, turquoise blue dyeings

of outstanding light fastness and excellent wet fastness properties are obtained.

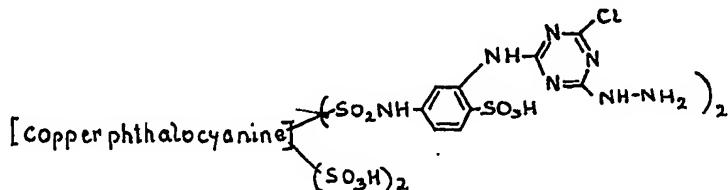
## EXAMPLE 2

A solution of 10 parts of cyanuric acid chloride in 100 parts of tetrahydrofuran is stirred into a mixture of 250 parts of ice and 150 parts of water. Then a neutralised solution of 33 parts of a dye of the formula:



in 500 parts of water is gradually added and the mixture stirred for about one hour at 0° to +5°C. Then a solution of 5 parts of hydrazine hydrate in 20 parts of water is introduced into the mixture and, after another hour, a solution of 12 parts of crystallised

sodium acetate in 20 parts of water. The whole is stirred for 15 hours at room temperature. The dye formed is salted out in the usual way, filtered off by suction, washed with aqueous sodium chloride solution and dried. The new dye has the following structure:



If cotton fabric is treated with this dye in the way described in Example 1, turquoise blue dyeing fast to wet treatment and light are obtained.

5 Similar dyes are obtained in an analogous way when starting from tetrakisamino copper phthalocyanine tetrasulphonic acid or bis-aminomethyl copper phthalocyanine disulphonic acid. By using equivalent amounts of the corresponding nickel or iron compound instead of the copper compound specified in the first paragraph of this example, and proceeding otherwise as explained in the first paragraph, turquoise blue dyes of somewhat more greenish shade are obtained.

EXAMPLE 3

A solution of 50 parts of the disodium salt of copper phthalocyanine disulphonic acid-( $\beta$ -aminoethyl)-amide disulphonic acid in 300 parts of water is allowed to flow gradually at 0° to +2°C into a suspension of 18 parts of cyanuric acid chloride in 200 parts of tetrahydrofuran and 250 parts of ice-water and the whole is thoroughly mixed with an impeller for one to two hours. The mixture is then stirred with a solution of 7 parts of hydrazine hydrate in 30 parts of water and then with a solution of 27 parts of crystallised sodium acetate in 50 parts of water. The whole is stirred at room temperature until the pH does not change any more. After a reaction period of about 20 hours, the solution is introduced into 2000 parts by volume of an aqueous saturated sodium chloride solution, the deposited dye filtered off and dried under reduced pressure at 30° to 35°C, or the filtered material made into a paste with ethanol, filtered off and dried in the air.

Cotton fabric is padded with an aqueous solution which contains in 1000 parts 20 parts of the dye described in the first paragraph, 50 parts of the dimethylol dihydroxyethylene urea and 5 parts of ammonium nitrate. The material is then squeezed out, dried at 60° to 70°C, heated for 5 minutes at 150°C, soaped and dried. A wet fast and light fast turquoise blue dyeing is obtained.

The copper phthalocyanine derivative used as initial material in the first paragraph of this Example is obtainable by reaction of 1 mol of copper phthalocyanine-3,3<sup>1</sup>,3<sup>11</sup>,3<sup>111</sup>-tetrasulphonic acid chloride with 2 mols of acetyl-aminoethylamine and saponification of the unreacted sulphonic acid chloride groups and the acetyl groups.

If 1 mol of copper or nickel phthalocyanine-3,3<sup>1</sup>,3<sup>11</sup>-trisulphonic acid chloride, monochlor copper phthalocyanine-3,3<sup>1</sup>,3<sup>11</sup>-trisulphonic acid chloride, copper phthalocyanine-4,4<sup>1</sup>,4<sup>11</sup>,4<sup>111</sup>- or -3,3<sup>1</sup>,4<sup>11</sup>,4<sup>111</sup>-tetrasulphonic acid chloride or nickel phthalocyanine-3,3<sup>1</sup>,3<sup>11</sup>,3<sup>111</sup>-tetrasulphonic acid chloride is reacted with 1 to 2 mols of acetylaminoethylamine, the acetyl compound saponified and the reac-

tion product obtained used as initial material, there are obtained in the manner described in the first paragraph of this Example similar dyes giving turquoise blue dyeings with similar properties.

EXAMPLE 4

25 parts of the dye obtained in Example 3, paragraph 1, are dissolved in 300 parts of water with the addition of dilute sodium carbonate solution at a pH of 7 to 7.5 and stirred with a solution of 10 parts of hydrazine hydrate in 20 parts of water. The alkaline solution is then heated at 90° to 95°C until the pH no longer falls.

The reaction product is salted out, filtered off and dried. A turquoise blue water-soluble dye is thus obtained which contains no chlorine.

By using methylhydrazine instead of hydrazine hydrate, a similar turquoise blue dye is obtained.

EXAMPLE 5

25 parts of the dye obtained in Example 3, paragraph 1, are dissolved in the way described in Example 4 and stirred with a neutralised solution of 10 parts of 1-amino-benzene-4-sulphonic acid in 50 parts of water. The whole is then heated to 90° to 98°C and a pH of about 7 maintained by adding dilute aqueous sodium carbonate solution. The mixture is allowed to stand for about 5 hours, the dye is salted out, filtered off and dried. The water-soluble dye is free from chlorine.

1-Aminobenzene-3-sulphonic acid, 1-amino-benzene-2,4-or-2,5-disulphonic acid or aniline may be reacted instead of 1-amino-4-sulphonic acid with similar results.

EXAMPLE 6

50 parts of tetraphenyl copper phthalocyanine trisulphonic acid-( $\beta$ -aminoethyl)-amide trisulphonic acid are dissolved in 500 parts of water at a pH of 7.0 to 7.5 and introduced with very rapid stirring at 0° to +5°C into a suspension of 18 parts of cyanuric acid chloride in 300 parts of ice-water in small portions. After remaining for 1 hour, the mixture is stirred with 35 parts of a 10% aqueous hydrazine solution and a pH of about 6 is maintained at room temperature by the addition of dilute aqueous sodium carbonate solution. After standing for 20 hours, the reaction product is salted out, filtered off and dried under reduced pressure at 40° to 50°C. A water-soluble dye is obtained which dyes cotton fast green shades in the presence of hardenable aminoplast-forming substances and acid-reacting compounds.

The compounds of the following formulae may be reacted in an analogous way instead of the tetraphenyl copper phthalocyanine derivative used in paragraph 1 of this Example. The dyes dye cotton in the shades indicated in the table:

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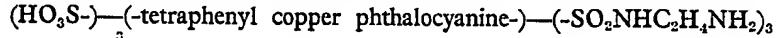
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formula	Shade on cotton
$(HO_3S)_2$ —(tetraphenyl copper phthalocyanine)— $(SO_2NH_2C_2H_4NH_2)_2$	green
$(HO_3S)_4$ —(tetraphenyl copper phthalocyanine)— $(SO_2NH-\text{C}_6\text{H}_3\text{NH}_2)_2$	green
$(HO_3S)_3$ —(tetraphenyl copper phthalocyanine)— $(SO_2NH-\text{C}_6\text{H}_4\text{NH}_2)_2$	green
$(HO_3S)_2$ —(tetraphenyl nickel phthalocyanine)— $(SO_2NH-\text{C}_6\text{H}_3\text{SO}_3H)_2$	green
$(HO_3S)_2$ —(diphenyl copper phthalocyanine)— $(SO_2NH_2C_2H_4NH_2)_2$	blue-green
$(HO_3S)_2$ —(diphenyl nickel phthalocyanine)— $(SO_2NH-\text{C}_6\text{H}_3\text{SO}_3H)_3$	blue-green

## EXAMPLE 7

A neutralised solution of 25 parts of the compound of the formula:



5 in 250 parts of water and a solution of 12 parts of the secondary condensation product from 1 mol of cyanuric acid chloride and 2 mols of hydrazine in 200 parts of water are mixed and gradually heated to 80° to 90°C.

10 A pH of 6 to 7 is maintained by adding dilute aqueous sodium carbonate solution. After a reaction period of several hours, the reaction product is salted out, filtered off and dried at a low temperature. A water-soluble green dye is obtained.

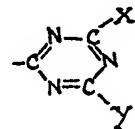
15 A similar dye is obtained by dissolving 25 parts of the dye obtained according to Example 6, paragraph 1 and 10 parts of hydrazine hydrate in 300 parts of water and heating for 8 hours at 90°C. This dye is salted out as usual filtered off and dried.

20 10 parts of one of the dyes obtained according to paragraph 1 or 2 of this Example are stirred into 100 parts of a 40% formaldehyde solution and, after adding 10% sodium hydroxide solution, stirred at a pH of 9 to 10 at room temperature for 24 hours. It is then salted out, filtered and dried at low temperature. Dyes containing methylol groups are

thus obtained which dye cotton fast green 30 shades.

WHAT WE CLAIM IS:—

1. Any tetrazaporphin dye, preferably soluble in water, which contains, attached by way of an amino group, at least one group of 35 the general formula:



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in which X denotes the radical of hydrazine or a hydrazine substituted by alkyl or acyl groups, and Y denotes a chlorine or bromine atom, a hydroxyl group, a sulphhydryl group, a sulphonate group, a primary, secondary or tertiary amino group, an ether group, a thioether group or the radical of hydrazine or a substituted hydrazine. 40

2. Dyes as claimed in claim 1 substantially 45

as described in any of the foregoing Examples.

3. A process for the production of dyes of the tetrazaporphin series wherein one mole of 2,4,6-tribromo- or trichloro-1,3,5-triazine is reacted at temperatures of up to 40°C in any sequence with (a) one mole of a tetrazaporphin dye, preferably soluble in water, containing at least one primary or secondary amino group, and (b) one mole of hydrazine or a hydrazine substituted by alkyl or acyl groups to form a binary condensation product.

4. A process as claimed in claim 3 wherein the halogen atom still present in the triazine ring of the resultant dye is exchanged for a hydroxyl group by hydrolysis, or for a sulphhydryl group, a sulphonate acid group, a primary- secondary or tertiary amino group, an ether or thioether group, a radical of hydrazine or substituted hydrazine by treatment at

temperatures of up to 100°C with a metal sulphite or a metal sulphide, ammonia, a primary or secondary amine, an alcoholate or a mercaptan, a hydrazine or a hydrazine derivative.

5. A process for the production of dyes of the tetrazaporphin series substantially as described in any of the foregoing Examples.

6. Dyes of the tetrazaporphin series when obtained by the process claimed in any of claims 3 to 5.

7. Textile materials which have been dyed or printed with a dye of the tetrazaporphin series as claimed in claim 1, 2 or 6 or with a methyol, esterified methyol or etherified methyol compound thereof.

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